RAFT Polymerization: A User Guide

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KEYWORDS

RAFT Polymerization, reversible addition-fragmentation chain transfer, reversible deactivation radical polymerization, controlled radical polymerization, living radical polymerization

ABSTRACT

This perspective summarizes the features and limitations of reversible addition-fragmentation chain transfer (RAFT) polymerization, highlighting its strengths and weaknesses, as our understanding of the process, both from a mechanistic and application point of view, has matured over the last 20 years. It is aimed at both experts in the field and new comers, including undergraduate and postgraduate students, as well as non-experts in polymerization who are interested in developing their own polymeric structures by exploiting the simple setup of a RAFT polymerization.

Introduction.

Since its first report in 1998,[1-3] the reversible addition-fragmentation chain transfer (RAFT) process has grown into one of the most versatile and powerful polymerization techniques for the synthesis of complex polymeric architectures. RAFT is a reversible deactivation radical polymerization (RDRP),[4] also known as living or controlled radical polymerization, a process that mimics closely the feature of living polymerization, whilst benefiting of the versatility of a radical process. RDRP enables the synthesis of polymeric architectures exhibiting predictable molecular weight, low molar mass dispersity ($Đ$), high end group fidelity and capacity for continued chain growth. The last 20 years have witnessed a rapidly growing interest in RAFT polymerization, initially focusing on the elucidation of the mechanism, then the demonstration of the myriad of polymeric architectures and functional materials that can be obtained from the process, and recently more application-driven reports. Today, with more than 8,000 publications (See Figure 1; noticeably, the seminal paper on RAFT by the CSIRO group is to date the most cited article in *Macromolecules*, with over 3,300 citations[5]), the RAFT process is a widely recognized polymerization technique, and it has been adopted by the wider scientific community, beyond polymer synthesis labs, as a tool to generate materials with a broad range of applications, from materials science to medicine.[6-9]

To date over 300 reviews have been published on RAFT polymerization, covering mechanistic understanding, polymer synthesis and the numerous applications of materials obtained by RAFT. With such a vast amount of literature, the RAFT process may appear a daunting topic to new comers and non-experts. This perspective aims at summarizing the system,

and is designed as both an overview and a tutorial on the RAFT process, in order to facilitate its adoption by the wider scientific community. For a detailed account of specific features of RAFT, the reader is referred to the more specialized reviews on the topic. This perspective will cover the fundamental of the mechanism of RAFT, and review the features and limitations of the RAFT process in terms of monomer class, molecular weight, synthetic process, and large scale industrial applications. It will not cover the range of materials obtainable by RAFT, in terms of architectures[10] (block,[11] star,[12] branched, hyperbranched, network,[13] stimuli responsive,[14] surface grafted[15] copolymers), nanoparticles and nanocomposites,[16] green and sustainable materials[17] and bioapplications;[18] the reader is referred to recent exhaustive reviews in these domains.

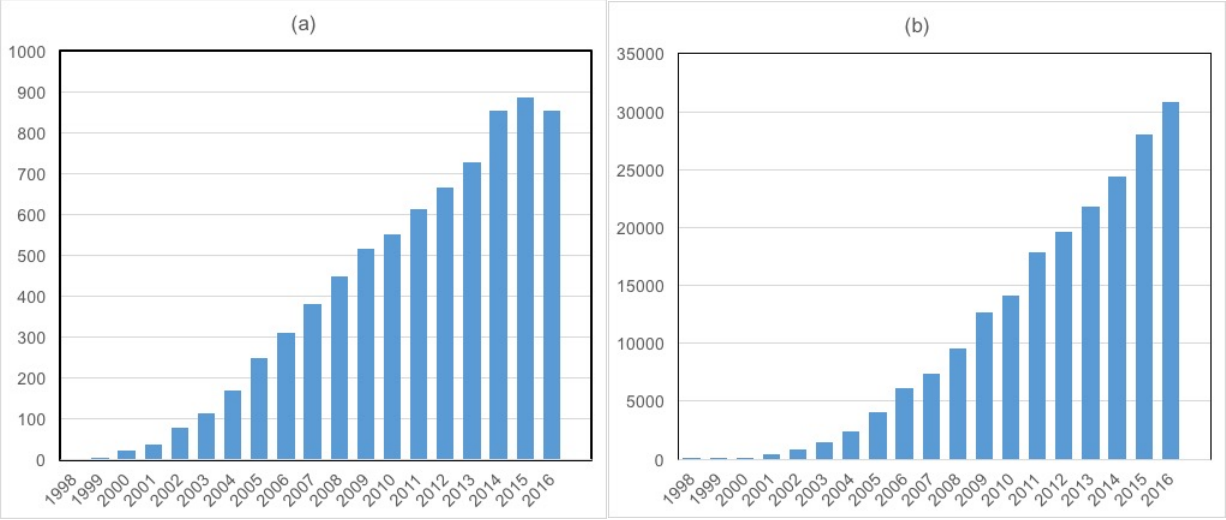
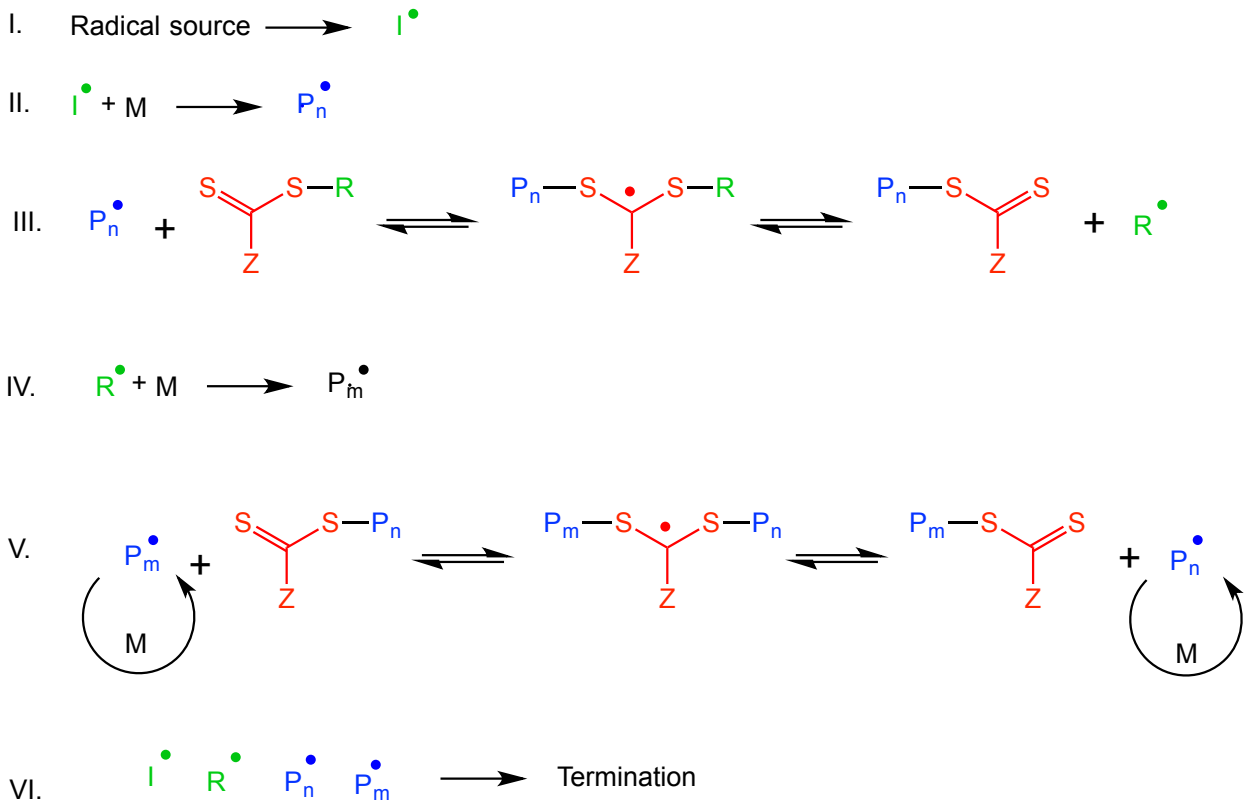


Figure 1. Published items per year (a) and citations per year (b) on "RAFT polymerization" and "reversible addition fragmentation chain transfer polymerization" – source Web of Science, March 2017.

1. The RAFT process

Mechanism. RDRP is based on an equilibrium between active and dormant chains, which can be achieved by one of two processes: (*i*) reversible deactivation (relying on the persistent radical effect (PRE),[19] *e.g.* nitroxide mediated polymerization (NMP)[20] and metal mediated living radical polymerization / atom transfer radical polymerization (ATRP)[21-22]), and (*ii*) degenerative transfer (*e.g.* RAFT).[23] In a degenerative transfer system, there is no change in the overall number of radicals during the activation-deactivation process, so a source of radicals is required, typically a radical initiator.

The RAFT mechanism is depicted in Scheme 1. Following activation (step I), the radical species add to the RAFT agent to enter equilibrium between active and dormant species (Step III and V). The chain transfers steps that form the basis of the RAFT mechanism are degenerate as they involve a reversible transfer of the functional chain end group (typically a thiocarbonylthio group, Z–C(=S)S–R) between the dormant chains (macroRAFT agent or macroCTA) and the propagating radicals. In an effective process, the rate of the equilibrium is higher than propagation, so there should be less than one monomer unit added per activation cycle, therefore all chains will have a similar degree of polymerization (DP) at a given time. The overall process comprises of the insertion of monomers between the R and Z–C(=S)S groups of a RAFT agent, which form the α and ω end group of the majority of the resulting polymeric chains.



Scheme 1. Proposed mechanism of reversible addition-fragmentation chain transfer polymerization.

A key requirement in RAFT, which is very different from other RDRP systems and also often misunderstood, is the use of a radical initiator. In degenerative transfer systems, a radical source such as a free radical initiator is advantageous as it allows tuning of the system in terms of polymerization rate and number fraction of living chains by an appropriate choice of polymerization conditions. Indeed, the number of chains that undergo bimolecular termination directly corresponds to the number of radicals initially introduced in the system, typically from decomposition of a radical initiator during the polymerization reaction. This aspect is key to the RAFT process, and often overlooked by non-experts. A direct implication of this mechanism is that, unlike for systems based on reversible deactivation such as ATRP and NMP, a bimolecular

termination event does not lead to a loss of a "living" chain end (the ω-end thiocarbonylthio end group), but the number of chains with the thiocarbonylthio end group remains the same throughout the polymerization regardless of the extent of termination. It follows that the number of dead chain can be predicted ahead of polymerization, and therefore controlled, by controlling the number of radicals introduced in the system. In the case of initiation by thermal initiator such as diazo or peroxide compounds, the number of dead chain in a RAFT material is known, based on the number of initiator that have decomposed in the time of the reaction.

The products of a RAFT polymerization are therefore chains with and without the thiocarbonylthio end group at the ω-end (living and dead chains, respectively). Note that in RAFT, a dead chain is therefore a product of reaction rather than side-reaction, since it directly arises from the introduction of one of the reagents, the source of radicals. In order to optimize livingness of the system, these species have to be minimized. In addition, there are two types of polymeric chains with regards to the nature of the initiation (α-end): chains initiated by the source of radicals (typically an initiator fragment), and chains initiated by the RAFT agent R-group. Remarkably, and unlike RDRP systems based on reversible deactivation, the relative numbers of these four families of chains can be predicted from the number of radicals generated from the initiator and the number of RAFT agent moieties, thus enabling to draw a clear picture of species present in the materials at the end of the polymerization (Figure 2). For instance, assuming termination occurs exclusively by disproportionation, the number of dead chains is equal to the number of chains generated from the initiator, and includes both chains with an initiator fragment and the RAFT R-group at the α-end.

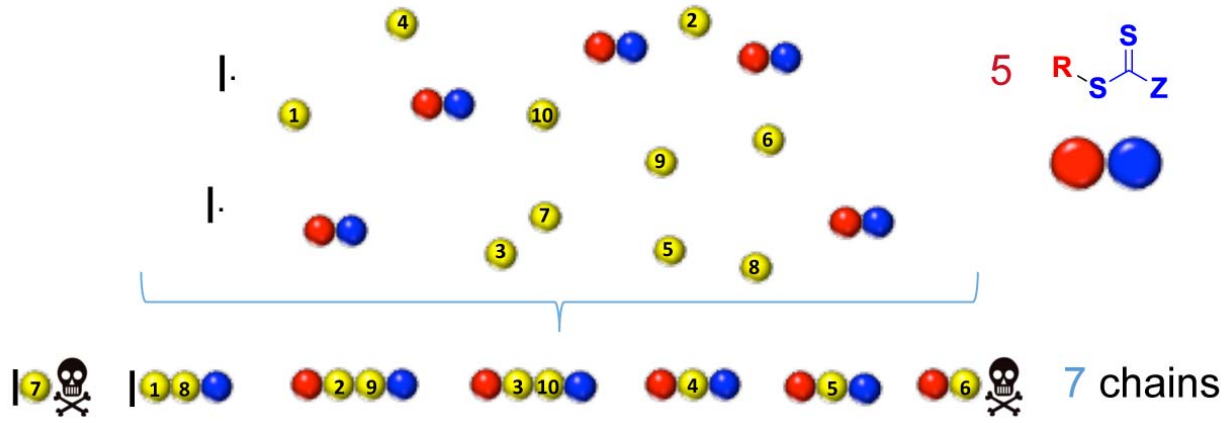


Figure 2. Schematic representation of the RAFT process. Two radicals (I·) are introduced in a system containing ten monomers (yellow) and five RAFT agents (red R group and blue Z–C(=S)S group). Polymerization leads to seven chains comprising two dead chains and five living chains. The livingness of the system L(%) is therefore 5/(5+2) x 100 = 71%. Note that dead chains may have the R group as α-end and conversely living chain may carry the radical functionality I as α-end.

Kinetics. Although reducing the initiator concentration in RAFT polymerization is therefore the key to optimize livingness of the system, a common misconception is to believe that it will also lower polymerization rate. The polymerization rate in the RAFT process in fact follows that of a conventional radical polymerization, and can therefore be manipulated by a number of parameters other than initiator concentration (see equation 1, here neglecting effects such as RAFT retardation often seen with dithiobenzoate RAFT agents[24-25] and effects of chain-length dependent termination[26]).

$$R_p(t) = k_p \times [M] \times \sqrt{\frac{f \times k_d \times [I]_0 \times e^{-k_d \times t}}{k_t}} \qquad (1)$$

where R_p is the polymerization rate, k_p the propagation rate coefficient, [M] the monomer concentration, f the initiator efficiency, k_d the decomposition rate coefficient of the initiator, $[I]_0$ the initial initiator concentration, and k_t the termination rate coefficient.

For instance, monomers with high propagation rate (high k_p) such as acrylamides, and initiators with high efficiency, or high decomposition rate (high k_d), can lead to fast polymerization rate whilst keeping low initiator concentration. In this case, the number fraction living chains (L, "livingness", given by equation 2) can also be kept to a maximum.

$$L = \frac{[CTA]_0}{[CTA]_0 + 2 \times f \times [I]_0 \times (1 - e^{-k_d \times t}) \times (1 - \frac{f_c}{2})} \quad (2)$$

where $[CTA]_0$ and $[I]_0$ are the initial concentrations of chain transfer agent and initiator, respectively. The term "2" means that 1 molecule of initiator gives 2 primary radicals with a certain efficiency f (typically 0.5 for diazo initiators). The term $1\text{-}f_c/2$ represents the number of chains produced in a radical–radical termination event with f_c the coupling factor ($f_c = 1$ means 100% bimolecular termination by combination, $f_c = 0$ means 100% bimolecular termination by disproportionation).

'Living' character. The ability of RAFT to produce 'living' chains, meaning here chains that can be extended by further monomer addition, differs greatly from other RDRP systems. Chain extension in RDRP processes based on reversible deactivation (e.g. NMP, ATRP, SET-LRP) typically requires the polymerization to be stopped at relatively low conversion (ca. 80%) during synthesis of the first block in order to maintain high livingness. The first block is then purified from residual monomer, for instance by precipitation, or dialysis. In RAFT, since the number of

dead chains is dictated solely by the number of radical species generated from the initiator, independently of monomer conversion, block copolymers can be prepared with 100% monomer conversion. Furthermore, in a reversible deactivation system such as NMP and ATRP, the polymerization cannot be left to continue when full conversion is reached, as living chains will gradually die as activation continues to generate active radicals that have a certain probability to terminate. This is not an issue for RAFT since the number of dead chains is only dictated by the number of radicals generated from the initiator. The introduction of initiator for each chain extension will of course result in the introduction of a small amount of homopolymer chains, due to the formation of new initiating species, but the exact number of these species can be calculated from the amount of initiator introduced, and therefore can be kept low. These conditions have enabled the synthesis of block copolymers at 100% conversion with number of blocks as high as 20.[27]

In summary, from a practical point of view, an optimal RAFT system requires a high rate of radical generation (considering k_d, for instance by using thermal imitator at temperatures higher than their 10h half-life temperature) and/or solvent-induced acceleration (thus giving a higher polymerization rate due to higher k_p). A large polymerization rate permits shorter polymerization time or lower amounts of initiator to reach full conversion.

2. Monomer class and RAFT agent

One of the key features of RAFT polymerization is its ability to polymerize an extensive range of functional monomers. Most vinyl monomers can be divided into two families based on their reactivity. 'More activated' monomers (MAMs) have their vinyl group conjugated to a

double bond (e.g. butadiene, isoprene), an aromatic ring (e.g. styrene, vinyl pyridine), a carbonyl group e.g. (meth)acrylates and (meth)acrylamides, maleic anhydride, maleimide), or a nitrile (e.g. acrylonitrile). 'Less activated' monomers (LAMs) exhibit double bond adjacent to oxygen, nitrogen, halogen, sulfur lone pairs or saturated carbons (e.g. vinyl acetate, *N*-vinyl pyrrolidone, vinyl chloride, 1-alkenes). RAFT enables control over polymerization of most monomers available to free radical polymerization. Exceptions mainly include monomers which functionality may undergo side reactions with the thiocarbonylthio group of the RAFT agent. Indeed, monomers containing nucleophilic substituents such as primary and secondary amines are typically more challenging, although they can still be used as long as reaction conditions are tuned, for instance by protonating the amino group.[28]

The vast majority of RAFT literature focuses on the controlled polymerization of (meth)acrylate, (meth)acrylamide and styryl derivatives, typically using dithioesters / dithiobenzoates or trithiocarbonate (see below). However, RAFT also provides control over the polymerization of monomers that are typically more challenging for RDRP techniques - for instance **vinyl acetate** and ***N*-vinylpyrrolidone** have been successfully polymerized using xanthates and dithiocarbamates CTAs (see below). The electron rich Z-groups in these CTAs donate electrons into the thiocarbonyl group, thus deactivating the thiocarbonyl towards radical addition, and destabilizing the RAFT intermediate radical. This promotes both monomer propagation and intermediate fragmentation. Furthermore, RAFT also offers some benefits when considering monomers that are challenging to polymerize by conventional free radical polymerization. **Ethylene** polymerization by a free radical process typically leads to high molecular weight materials with large $Đ$, due to branching via backbiting. However, the use of RAFT mediated by xanthates as controlling agents at 70 ºC and 200 bars dramatically reduce

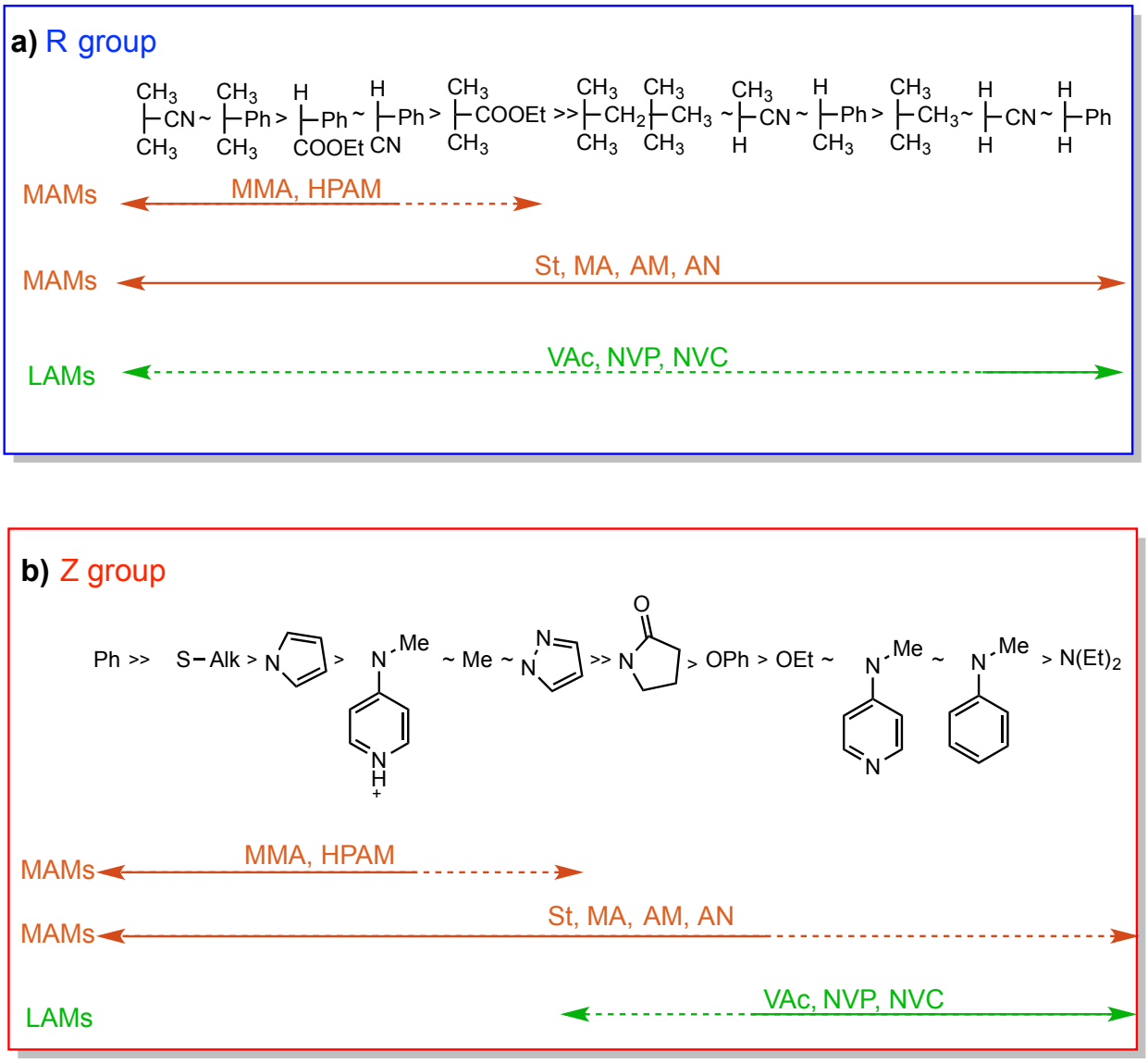
branching reactions ($Đ$ ~1.5-2), enables the introduction of functional groups within the PE chains via incorporation of up to 10 mol % VAc comonomer, and permit chain extension of the PE chain.[29] Similarly, whilst the free radical polymerization of **dienes** (e.g. butadiene, isoprene, chloroprene) typically leads to crosslinking relatively early in the reaction, RAFT enables to reach much higher conversions before gelation of the system.[30] Optimal RAFT agents are trithiocarbonates and dithioesters. Polymerization can be performed in solution at temperature above 90 ºC, or in emulsion, at lower temperatures (above 65 ºC). A better control is also obtained in emulsion polymerization whereby an amphiphilic macroRAFT agent is used to both mediate the polymerization and replace the surfactant (see process section below).

The versatility in monomer compatibility of RAFT arises from the reactivity of the CTA. The key aspect of a successful RAFT polymerization is to ensure that the C=S bond is more reactive to radical addition than the C=C bond of the monomer, and this is obtained by careful selection of the Z and R group. The Z group is mostly responsible for the reactivity of the C=S bond towards radical addition and governs the stability of the intermediate radical, which has to be considered relatively to the reactivity of the propagating radical. Due to the electronic stabilization from their substituent, often coupled with steric factors, MAMs produce relatively more stabilized radicals and therefore require a Z group that will help with the stabilization of the intermediate radical to favor radical addition on the C=S. Therefore, trithiocarbonates (Z = *S*-alkyl) or dithiobenzoates (Z = Ph) CTAs are typically selected to control MAMs polymerization. On the other hand, the high reactivity of LAMs make them poor homolytic groups, and they require intermediate radicals less stable, such as xanthates (Z = *O*-Alkyl) or dithiocarbamate (Z = *N*-alkyl), in order to favor fragmentation of the propagating radical, as a more stable intermediate acts as radical sink and prevents polymerization. The lone pair of electrons on oxygen

(xanthates) and nitrogen (dithiocarbamates) is delocalized in the thiocarbonyl group and therefore deactivates the C=S bond towards radical addition and destabilize the radical intermediate. This effect therefore promotes propagation and intermediate fragmentation, thus enabling control over polymerization of LAMs, but poor control over polymerization of MAMs.

The role of the R group is much more subtle and affects the RAFT through: 1/ radical addition to the CTA, since the *S*-R group influences the C=S activity in a similar way as a *S*-alkyl Z group; 2/ subsequent fragmentation from the intermediate formed, as the R group has to be a good leaving group to fragment and 3/ propagation, since the R group has to rapidly reinitiate propagation to ensure all chains are initiated in the same time frame to obtained narrow molecular weight distribution. Thus a fine balance between radical stability and steric effects (the R group has to form a radical stable enough to be formed, but not too stable so that it can add to a monomer) has to be met. Typically, good R groups are groups that mimic monomer radicals, or thermal initiators such as AIBN.

General guidelines for the selection of Z and R group, adapted from previous publications,[31] are shown in Scheme 2.



Scheme 2. a) Guidelines for selection of the R group of RAFT agents (Z–C(=S)S–R) for various polymerizations. Transfer coefficients decrease from left to right. Fragmentation rates also decrease from left to right. A dashed line indicates partial control (i.e., control of molar mass but poor control over dispersity or substantial retardation in the case of VAc, NVC, or NVP). **b)** Guidelines for selection of the Z group of RAFT agents (ZC(=S)SR) for various polymerizations. Addition rates decrease and fragmentation rates increase from left to right. A dashed line indicates partial control (i.e., control of molar mass but poor control over dispersity

or substantial retardation in the case of LAMs such as VAc or NVP). Adapted from ref. [31]. Abbreviations: MMA – methyl methacrylate, HPMAM – N-(2-hydroxypropyl) methacrylamide, St – styrene, MA – methyl acrylate, AM – acrylamide, AN – acrylonitrile, VAc – vinyl acetate, NVP – N-vinylpyrrolidone, NVC – *N*-vinylcarbazole.

R group consideration also directly affects block copolymer synthesis through sequential monomer addition, when the R group represents a polymeric chain made of the first monomer to be polymerized (i.e. the RAFT agent is a macroCTA). As in most RDRP systems, the order of monomer addition is key to good control over block copolymer synthesis, and the poly(MAM) has to be synthesized first if using a bulk system, as poly(LAM)s are comparatively poorer leaving groups. In order to polymerize LAMs first, a monomer starve-feed process has to be used, to artificially increase the chain transfer constant of the poly(LAM) macroCTA towards MAMs.[32]

Although these considerations may seem complex, relatively good control (i.e. $Đ$ between 1.05 and 1.3) of most types of monomers can be achieved with a handful of chain transfer agents.

Aromatic dithioester (e.g. dithiobenzoates) offer best control over polymerization of MAMs monomers, but they are also relatively unstable in time, and prone to side reactions such as hydrolysis. They also lead to retardation of certain monosubsituted MAMs and almost completely inhibit LAMs polymerization.

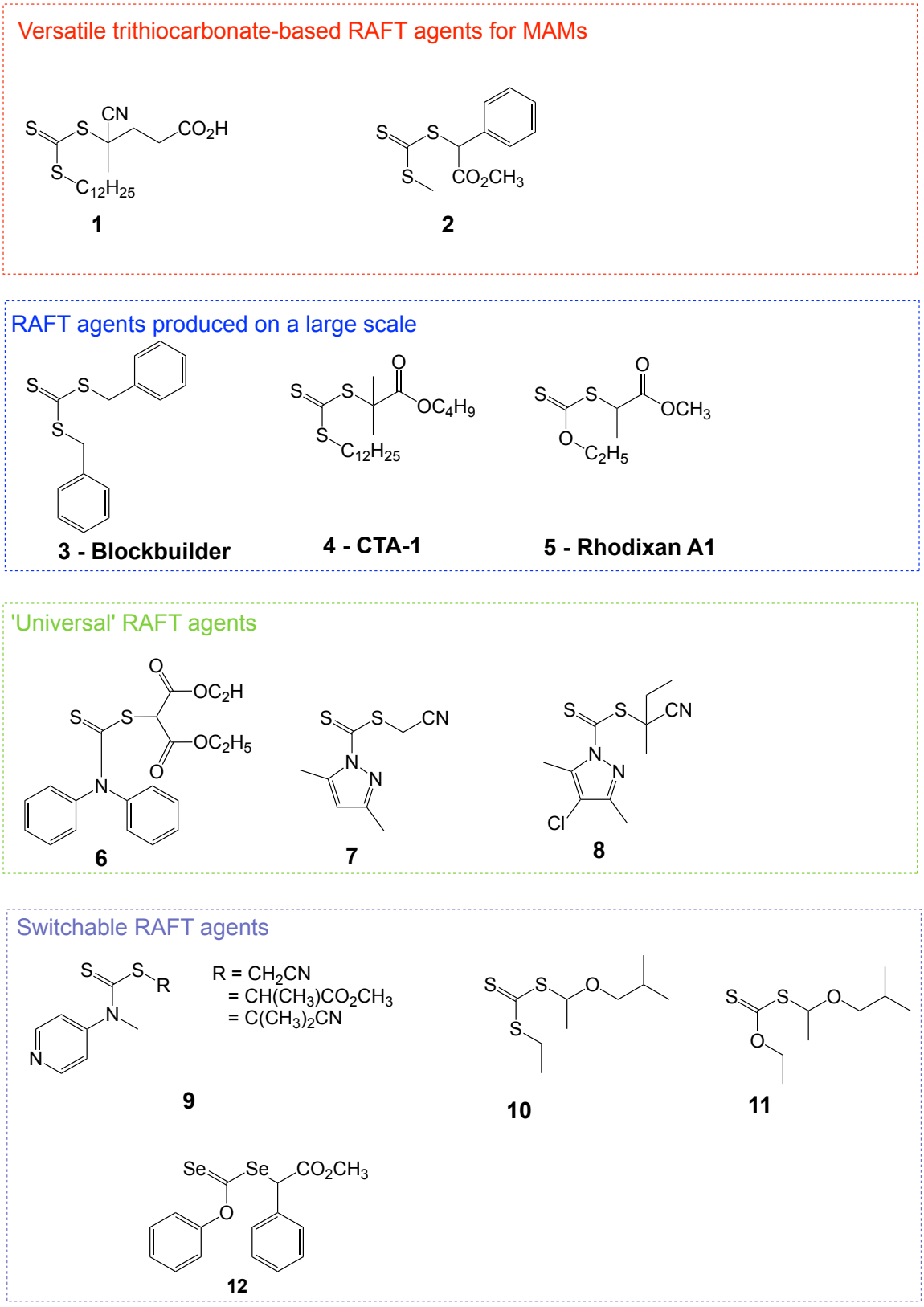
Trithiocarbonates are the most popular CTAs for polymerization of MAMs, as they balance activity and stability, and can be obtained from simple synthetic procedures. The most versatile trithiocarbonates in terms of monomer range are those with a tertiary R such as the commercially

available 2-cyano-2-propyl dodecyl trithiocarbonate (Scheme 3, **1**). *S*-Methoxy carbonylphenylmethyl methyltrithiocarbonate (Scheme 3, **2**) is a less known yet very versatile trithiocarbonate CTA, which also enables functionalization of hydroxyl and amine containing compounds.[33] Other noteworthy trithiocabonate CTAs include Arkema's Blocbuilder DB[34] (Scheme 3, **3**) and Lubrizol's CTA-1[35] (Scheme 3, **4**), both enabling controlled polymerization of most MAMs (typically in batch mode, although methacrylate derivatives require a monomer feeding process).

Xanthates and dithiocarbamates, often overlooked in MAMs polymerization, are intermediate CTAs that can provide very good control over LAMs polymerization and relative control of the polymerization of MAMs. **Xanthates** can lead to well controlled block copolymers ($Đ \sim 1.2$) of the MAMs that display higher activity (e.g. acrylamides and acrylates[36]) and LAMs (e.g. vinyldiene fluoride,[36] vinyl acetate,[37] DADMAC, [38]and N-vinyl pyrrolidone[39]). The Rhodia-developed Rhodixan A1 (Scheme 2, **5**) is a good example of such a versatile xanthate. **Dithiocarbamates** are also very versatile CTAs, which control over MAMs also include acrylates and acrylamides, and can be extended to styrene, whilst still controlling LAMs such as vinyl acetate.[40] Although $Đ$ is not as low as equivalent polymeric chains obtained from trithiocarbonates or dithiobenozates, (typical $Đ$ for dithiocarbamates ranges from 1.2 to 1.4), the control is more than sufficient for most application, and it allows to generate block copolymers of MAMs and LAMs in a simple one-pot process. The key structural design of an effective dithiocarbamate as universal RAFT agent is to conjugate the lone pair of electrons of the nitrogen atom with carbonyl or aromatic groups. For instance, **6** (Scheme 3) enables the formation of a block copolymer of styrene and vinyl acetate by sequential monomer addition.[41]

Scheme 3 provides structure of CTAs that have shown good overall control over both MAMs and LAMs, and their block copolymers.

Finally, it is worth noting here the use of macromonomers (ZC(=C)CR, obtained by catalytic chain transfer polymerization) as possible chain transfer agents, first reported by the CSIRO group in 1996, and considered as the 'original' RAFT agents.[42-43] Although they have very low chain transfer constant, and are therefore poor RAFT agents in a conventional process, the C_t can be artificially increased, for instance by feeding monomer or by using emulsion polymerization. This approach was elegantly optimized recently to generate multiblock copolymers of methacrylic monomers.[44]



Scheme 3. Structures of popular RAFT agents.

If a more refined control over *Đ* is required, slight modulation in the Z group structure is necessary. For instance, CTAs containing a **pyrazole** as Z group, such as that in the commercially available cyanomethyl (3,5-dimethyl-1H-pyrazole)-carbodithioate[45] provides good control over a variety of MAMs and LAMs, including acrylates, acrylamides, styryl derivatives, and vinyl acetate, with *Đ* ranging 1.1 to 1.3 (Scheme 3, **7)**. This control does not extend to methacrylates, which require a variation in Z group, and a tertiary R group, 2-cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate (scheme 3, **8**).[45]

An alternative approach to the control of monomer of very different reactivity that also employs the versatility of dithiocarbamates is to use a 'switchable' RAFT agent – a CTA which reactivity (and chain transfer constant) can be modulated based on external conditions. An elegant example is the pH-switchable *N*-aryl-*N*-(4-pyridinyl)dithiocarbamates RAFT agent reported by the CSIRO team,[46] which reactivity is changed by protonation of the pyridine ring in the Z group of a dithiocarbamate (Scheme 3, **9**). Whilst the C=S bond of the neutral CTA has low reactivity and the intermediate fragments faster, thus promoting control of LAMs polymerization (VAc, NVP, NVC, *Đ* ~ 1.1-1.2), protonation of the pyridine ring in presence of a strong acid (e.g., 4-toluenesulfonic acid, trifluoromethanesulfonic acid) or a nonprotic Lewis acids (e.g. aluminum triflate) activates the C=S bond and favors control of MAMs polymerization (butyl acrylate, dimethylacrylamide, styrene, *Đ* ~ 1.1-1.2).[46-49] This feature becomes very useful when synthesizing block copolymers poly(MAM)-*b*-poly(LAM), by switching the RAFT agent after synthesis of the first block. Note that these CTAs are however intrinsically very sensitive to acids and it is important that no acid remains when switching to polymerise LAM or poor control is then observed. In addition, the dependence on acid/base to switch the reactivity limits applications.

An alternative switchable RAFT agents is the use of a radical initiator and a Lewis acid to activate the Z–C(=S)S–R group of xantahtes or trithioesters into radical and cationic species, respectively, thereby inducing interconvertible radical polymerization of acrylates (MAMs, e.g. using **10**, Scheme 3) and vinyl acetate (LAMs, e.g. using **11**, Scheme 3) and cationic polymerization of vinyl ethers (LAMs, e.g. using either **10** or **11**). This approach can be used to generate pol(MAM)-*b*-poly(vinyl ethers) with *Đ* ranging 1.2-1.3.[50-53]

It is also worth mentioning the use of heteroatoms to substitute sulfur in RAFT agents. Substituting S by Se in RAFT agents such as trithiocarbonates,[54] dithiobenzoates[55] or dithiocarbamates[56] does not affect the reactivity of the CTA, except in the case of methyl 2-(phenoxycarbonoselenoylselanyl)-2-phenylacetate (Scheme 3, **12**) which leads to remarkable control (*Đ* ranging 1.1-1.3) of MAMs (methyl methacrylate, butyl acrylate, methyl acrylate, pentafluoro styrene, NIPAM, *N*-vinylcarbazole) and LAMS (vinyl acetate),[57] and enable the synthesis of their block copolymers. Similarly, the use of phosphorous (thiophosphinoylcarbodithioates)[58] and metallophosphorous (Cr, Mo pentacarbonyldiphenylphosphinocarbodithioate complexes[59] and W diphenyl(dithioformato)phosphine complexes[60]) derivatives as Z group provides CTA with similar reactivity to that of the corresponding thiocarbonylthio group when polymerizing styrene and acrylate derivatives.

Although a number of elegant solutions has been proposed to control both MAMs and LAMs with a single CTA, to date no single RAFT agent offers good control over both methacrylates and LAMs.

3. End-group modification

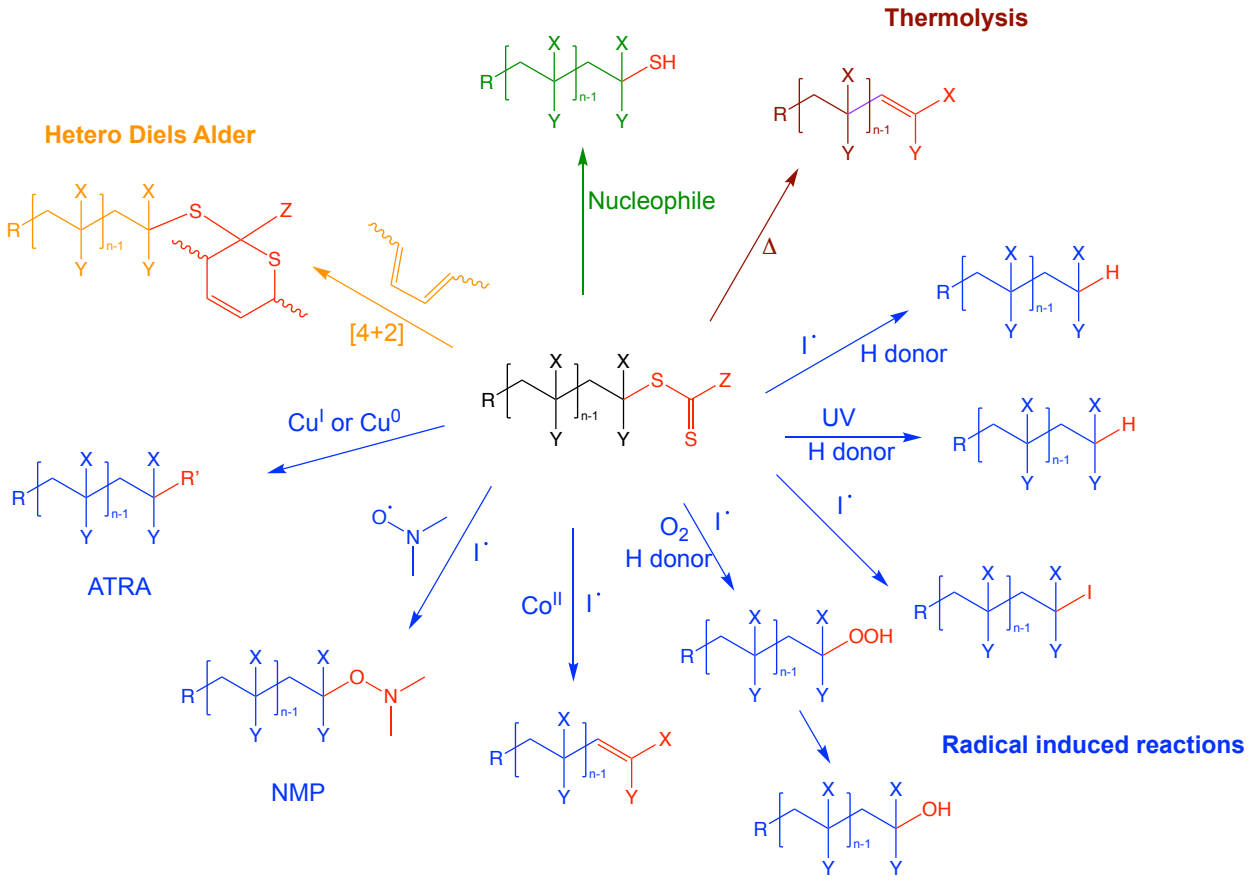
The thiocarbonylthio group is also a very versatile functional group, which can either be exploited for polymer chain-end functionalization, or might need to be removed for certain applications.[61] Initial concerns with the end group of a RAFT polymer were linked to the color of polymers obtained by RAFT, especially as early work focused on the use of dithiobenzoates that impart a pink color to the resulting polymer. Color is now less of an issue when trithiocarbonates (yellow) or xanthates and dithiocarbamates (pale yellow to colorless) are used. Thermal and chemical stability of the RAFT end group can however be of concern, and depending on applications, its removal is warranted. Beyond simple end group removal, the reactivity of the thocarbonyl thio group can also be exploited to add chain end functionalities to polymers obtained by RAFT.[62-63]

A feature of the thiocarbonylthio end group is that it can be used as a masked thiol, and its reduction to a thiol, by either hydrolysis or aminolysis, opens up a number of nucleophilic or radical functionalization. This process is one of the most commonly encountered end group functionalization of a RAFT polymer. However, care needs to be taken with reaction conditions as side reactions of this transformation include formation of disulfide bridges between polymer chains, thus a strong reducing agent should also be used, or in the case of poly((meth)acrylate)s, back-biting of the thiol moiety on the ester pendant group of the repeating units which leads to a thiolactone end-groups.[63]

Complete removal of the thiocarbonylthio group can also be required, and the most effective processes are either thermolysis or radical induced transformation.[63] Thermolysis, with temperature ranging 150-250 ºC, is a simple and powerful method for total end group removal and introduction of an alkene at the polymer chain end, but the mechanism of reaction depends on both the polymer and the type of thiocarbonylthio group. Removal of trithiocarbonates from

poly(acrylate)s or polystyrene, xanthates from polystyrene and poly(vinyl acetate) and dithiobenzoate from poly(methacrylate)s have been shown to proceed effectively.[63] Radical induced transformation is more versatile, as it provides a mean of both end group removal and potential alternative chain end functionalization. The process employs the reactivity of thethiocarbonylthio end group towards a radical generated *in situ* (e.g. thermal initiation) followed by its fragmentation,[63-64] or reduction using a metal catalyst (e.g. Cu(I) or Cu(0)) in a process of atom transfer radical addition,[63] or long-wave ultraviolet irradiation that leads to photolytic cleavage of thethiocarbonylthio end group,[65] to generate a propagating radical. In absence of monomer but in presence of either a radical trap (e.g. radical initiator)[64] or hydrogen donor,[63] the radical is trapped by a functional group or hydrogen, respectively. This straightforward procedure enables removal of trithiocarbonate, dithiobenzoate, xanthate and dithiocarbamate end groups, and is efficient for polymers derived from most MAMs and LAMs.

It should be noted however that from a practical perspective,thiocarbonylthio group removal often requires further purification of the polymer to separate from the end group removed, which can be problematic for larger scale productions. In this case, thethiocarbonylthio group is maintained at the end of the polymeric chain. Scheme 4, adapted from ref. [63] provides an overview of the various reactions enablingthiocarbonylthio group transformation.



Scheme 4. Most commonly used paths tothiocarbonylthio end group modification grouped by types of reaction. Adapted from ref. [63]

4. Molecular weights

One of the well-known limitations of RDRP systems is the limited range of molecular weights achievable whilst keeping control over dispersity and end group functionality, ranging from oligomers to a few 100,000's of g/mol. In a RDRP system based on reversible deactivation (e.g. NMP and ATRP), the higher the targeted degree of polymerization (DP), the longer the cumulative time the growing chain spends as a propagating radical, and consequently the higher is the probability that termination, or other side reactions leading to destruction of the radical

chain end, will stop the growth of the chain.[23, 66-68] In RAFT, the number fraction of living chains at the end of the polymerization decreases with increasing target DP: since at a given concentration in radical source the number of dead chains is constant independently of other parameters, including targeted DP, the lower the targeted DP (typically calculated from the $[M]_0/[CTA]_0$,), the higher is the concentration in CTA, thus the higher is the absolute number of living chains. It follows that RAFT is an ideal technique for the synthesis of low molecular weights oligomers of controlled molecular weights. Control over low molecular weight polymers is an advantage of RAFT over reversible deactivation RDRP systems for which, due to the persistent radical effect, control tends to increase with increasing conversion and thus increasing molecular weight.[69-70] In RAFT, $M_{n,th}$ is given by eq 3:

$$M_{\mathrm{n,th}} = \frac{[\mathrm{M}]_0 \times p \times \mathrm{M_M}}{[\mathrm{CTA}]_0 + 2 \times f \times [\mathrm{I}]_0 \times \left(1 - e^{-k_\mathrm{d} \times \mathrm{t}}\right) \times \left(1 - \frac{f_\mathrm{c}}{2}\right)} + \mathrm{M_{CTA}} \qquad (3)$$

where $[M]_0$, $[CTA]_0$ and $[I]_0$ are the initial concentrations of monomer, chain transfer agent and initiator, respectively, p is the monomer conversion, M_M and M_{CTA} are the molar masses of monomer and chain transfer agent, respectively.

Practically, this equation is simplified to eq 4:

$$M_{\mathrm{n,th}} = \frac{[\mathrm{M}]_0 \times p \times \mathrm{M_M}}{[CTA]_0} + \mathrm{M_{CTA}} \qquad (4)$$

RAFT routinely provides excellent control over polymeric chains of molecular weight ranging 1,000's to 100,000's g/mol. Higher molecular weight, so called ultra-high molecular weight (UHMW) polymers are also accessible, but require more specific reaction conditions, based on kinetic parameters. Indeed, UHMW polymers require monomers with high propagation rate by comparison to termination rate. Referring to equation 1 above, accelerated polymerization (high R_p) can be achieved by using high monomer concentration (3-5M),

initiators with high efficiency or high decomposition rate (see above), and polar solvents, which are known to stabilise the transition state of propagating radicals by thus lowering their activation energy.[71] Lower termination rates can be achieved by reduced temperatures, reduced radical concentration, and high monomer concentrations (high solid content, which leads to a medium of high viscosity, thus limiting termination events[72]).

These conditions can be reached for water-soluble polymers by selecting high k_p monomers such as acrylamide derivatives, polymerised in water (which is known to increase k_p of water-soluble vinyl monomers capable of forming hydrogen bonds[71]), at high monomer concentrations (*ca*. 5M, to increase polymerization rate R_p and medium viscosity), whilst working at low temperature (10-20 °C) and low concentration in radicals to lower termination rates. This approach leads to the formation of polymers with molecular weight up to 10^6 g/mol.[73] An alternative approach to reducing termination in these systems is the use of UV and visible-light irradiations for the photolytic cleavage ofthiocarbonylthio group, thus removing the need of a radical source such as thermal initiators. Photolysis of the C-S bond leads to a propagating polymeric radical and a radicalthiocarbonylthio group, which can reversibly terminate the propagating chains, following the mechanism of iniferters.[74] The control over molecular weight is therefore achieved through a combination of degenerative chain transfer and reversible deactivation. Such source of radical formation avoids the continuous generation of low-molecular-weight radicals from conventionally used free radical initiators, which can terminate polymerization by coupling with high-molecular-weight chains. Photolysis of thethiocarbonylthio group generate radicals of high molecular weights, which in viscous conditions are less ikely to terminate, therefore slowing rates of termination. With this approach,

molecular weights in the range of 1-10 10^6 g/mol ($Đ$ ranging 1.1-1.4) can be achieved using trithiocarbonates and xanthates.[75]

For hydrophobic monomers, emulsion polymerization is an effective process to reach UHMW, as it allows for high polymerization rate and reduced side reactions, due to the segregation effect (compartmentalization in nanoreactors) resulting in lower rates of bimolecular radical termination. In RAFT emulsion polymerization, an amphiphilic RAFT agent is used in place of the surfactant, thus promoting controlled polymerization in the polymer particles (*ab initio* emusion, see process section below). In addition of being an industrially relevant process, RAFT emulsion also enables UHMW polymers (10^6 g/mol, $Đ \sim$ 1.2-1.3) and block copolymers from typically slow propagating monomers such as styrene.[76-77]

A noteworthy, although more specialized approach to UHMW polymers is the use of very high pressure to increase polymerization rate. For instance, the polymerization of methyl methacrylate was mediated by a dithiobenzoate at 5 to 9 kbar to yield polymers of molecular weight 10^6 g/mol and $Đ \sim 1.1$.[78]

5. Radical sources

Thermal initiation. The source of radicals in RAFT is key to the process, in terms of (a) control, since the number of radicals generated determines the amount of dead chains in the system, (b) polymerization rate, as it is directly related to radical concentration, and (c) reaction conditions (e.g. appropriate reaction temperature, process, etc.). Typically, a thermal initiator is used, either diazo compounds or peroxides, or in some cases thermal autoinitiation, as in the case of styrene, is preferred.

A common misconception in degenerative transfer radical polymerization processes such as RAFT is that the need of an external source of radicals leads to lower chain end retention than for polymerization techniques based on deactivation by reversible deactivation. [68,79] In addition, it is commonly believed that *initiator* concentration, rather than *radical* concentration, will impact on the polymerization rate. It follows that typical reaction setups try to balance speed of reaction and livingness of the resulting polymeric chains by controlling initiator concentration (or more specifically, CTA : Initiator ratio, typically ranging 5-10). However, it is clear from equation 1 that the polymerization rate can be manipulated via a number of parameters other than the initiator concentration, independently of the livingness of the system. Indeed, the number of dead chains is solely dictated by the *number* of radicals generated throughout the polymerization, the *rate* at which these radicals are generated does not influence the livingness. Therefore, the polymerization rate can be increased by an increase in *the rate of radical generation*, e.g. by using an initiator possessing a high k_d, without affecting livingness. For instance, 4,4′-Azobis(4-cyanovaleric acid) (ACVA, half-life time of 10 h at 69˚C)[80] undergoes 85% decomposition in 24 h at 70˚C in water, versus 95% decomposition in 2 h under the same conditions for 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, half-life time of 10 h at 44˚C). It follows that a successful RAFT polymerization can be performed with VA-044 as initiator with a ratio CTA : VA-044 as high as 400, and reach quantitative (99%) monomer conversion in 2 hours, with 99% of chains still living.[27, 80-81] Such conditions are ideal for the generation of (multi)block copolymers, at near complete monomer conversion.[27, 80-85]

However RAFT is not limited to thermal initiation, and can be mediated by any source of radicals, as a conventional radical process. Recent studies have shown that RAFT can be conducted using a range of radical sources.

Redox initiation. Frequently used for industrial free-radical polymerization, either in aqueous solution or emulsion, redox initiation is easy to handle, and can be performed using inexpensive, metal-free oxidising and reducing agents. Aqueous redox-initiated RAFT polymerization can be used to allow the controlled polymerization of a range of water soluble acrylate and acrylamide monomers with good control ($Đ \sim 1.2$-1.3),[84] and its use at room temperature enables the aqueous synthesis of polymers exhibiting a lower critical solution temperature such as polymers from NIPAM,[86] *N*-Vinyl pyrrolidone[87] and *N*-acylated poly(aminoester)-based comb polymers.[88-89] Ambient temperature polymerization also limit side reaction of transfer/branching normally observed in acrylate monomer polymerization at elevated temperature[84] and also permit to obtain ultra-high molar mass polyacrylamido polymers (see above).[73] The redox pair tert-butyl hydroperoxide/ascorbic acid (TBHP/AsAc) is a suitable redox couple, enabling full monomer conversion at 25 °C whilst keeping high chain end retention, although reactions are slow and can take up to 24 h. In these conditions, multiblock copolymers showing mixture of acrylate and acrylamide blocks, and with block number varying from 4 to 8, can be prepared, with a final dispersity below 1.3.[84]

Light induced initiation. Photo-controlled RAFT is typically performed at room temperature, and enables to switch 'on' and 'off' the reaction, as well as controlling spatially a RAFT polymerization.[90-92] There are typically two approaches to inducing RAFT polymerization via light activation, either by direct photodissociation of the thiocarbonylthio compound, thus without addition of a photoinitiator and following the iniferter mechanism,[74] or by photoinduced electron-transfer (PET) process.

Photodissociation RAFT follows the mechanism of iniferter polymerization where light irradiation, typically UV, cleaves the thiocarbonylthio group from the R group / propagating chain, to generate an active radical which then enters the RAFT equilibrium. The process has been applied to dithiocarbamates (the original iniferters) and xanthates for LAMs and dithioesters (including dithiobenzaotes) and trithiocarbonates for MAMs.[90-91] This process relies heavily on irradiation time, conversion (high conversions are typically difficult to achieve) and thethiocarbonylthio compound structure, which dictates the wavelength required by the UV source. Recently it was shown that low light intensity and long-wavelength UV irradiation provides greater control over polymerization, also enabling high conversions to be reached for fast propagating monomers such as acrylamides.[93] Ultra high molecular weight polymers from fast propagating monomers such as acrylamides can also be obtained by this process.[75] Blue light irradiation was also successfully applied to the controlled polymerization of acrylates and acrylamides mediated by trithiocarbonates ($Đ \sim 1.1$),[94] of methacrylates mediated by a trithiocarbonate[95] and vinyl acetate mediated by xanthates.[96]

Photoactivation of the RAFT process, either via the use of a photoinitiator or via the use of a photoredox catalyst (so called photoinduced electron-transfer (PET) RAFT) is also possible. In the first case, the photoinitiator provides the source of radicals, similar to thermal initiation. This approach is somewhat complicated by the possible activation of the thiocarbonylthio group under similar wavelengths as those used to activate the photoinitiator. More versatile is PET-RAFT,[97] which employs a photoredox catalyst, activated by visible light (thus avoiding direct thiocarbonylthio photolysis) proposed to reduce the thiocarbonythio compound to generate a radical anion. The resulting radical anion fragments to give a propagating radical, before electron transfer regenerates the dormant polymer chain and the photocatalyst in its ground state.

'Simple' back-of-the-envelope-calculations show that when considering the extreme case of a single monomer insertion, PET-RAFT reversible dissociation alone cannot regulate molar mass, and the process relies on the activation-deactivation process of RAFT (i.e. a high transfer constant of the RAFT agent (or macro RAFT agent) is required), see for instance supporting information of reference [98]. PET-RAFT has been shown to be widely applicable to a variety of catalysts, including metallo-complexes (*fac*-[$Ir(ppy)_3$], $Ru(bpy)_3Cl_2$, chlorophyll A and zinc porphyrins) and organic compounds (e.g. the dye Eosyn Y, the photocatalyst 10-phenylphenothiazine and some tertiary amines). PET-RAFT has dramatically expanded the potential of light-induced RAFT polymerization by enabling controlled polymerization under visible light of a wide range of LAMs and MAMs, notably including methacrylate derivatives, whilst maintaining excellent chain-end fidelity, thus enabling multiblock copolymer synthesis.[94, 97, 99] PET-RAFT was also shown to produce oligomers by inserting monomers one unit at a time, although the process was limited to trimers, and depends heavily on both the choice of the RAFT agent, and the type of monomers.[98] Monomer type and the sequence of addition has to be carefully selected to ensure full fragmentation of the leaving group, yet single unit addition – this is achieved by considering the reactivity of the leaving groups relative to each other, and rate of propagation. For instance a trimer based on styrene derivatives, maleimide and VAc (or limonene) was designed. Although the process is limited in terms of types of monomer, it is a remarkable example of controlled single unit monomer insertion achieved by a radical process.

Figure 3, adapted from reference [91], provides an excellent summary of the various monomers, thiocarbonylthio compounds, activators, and light sources investigated to date for photo-controlled RAFT.

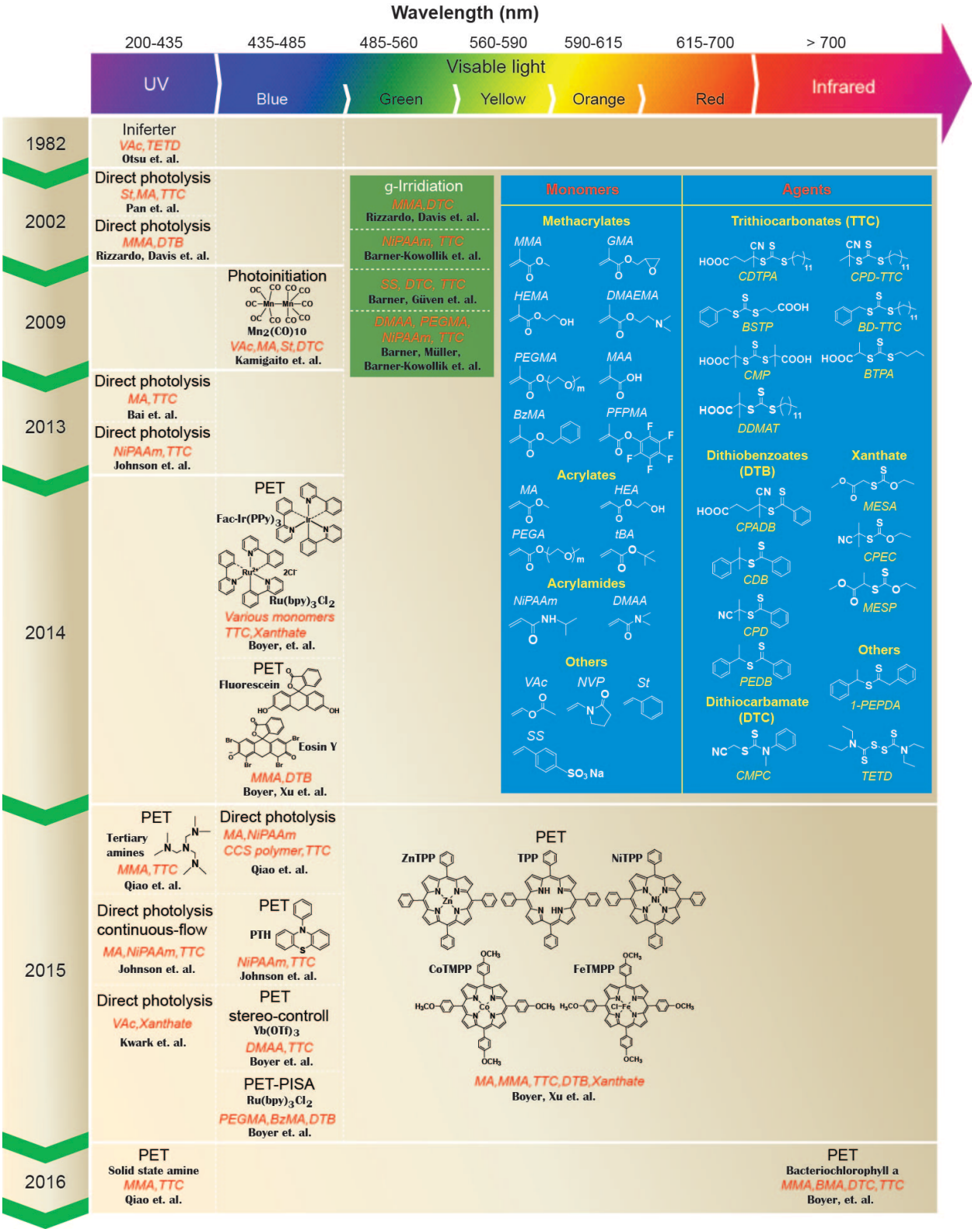

Wavelength (nm)
200-435
435-485
485-560
560-590
590-615
615-700
> 700
UV
Visable light
Blue
Green
Yellow
Orange
Red
Infrared
1982
Iniferter
VAc,TETD
Otsu et. al.
2002
Direct photolysis
St,MA,TTC
Pan et. al.
Direct photolysis
MMA,DTB
Rizzardo, Davis et. al.
g-Irridiation
MMA,DTC
Rizzardo, Davis et. al.
NiPAAm, TTC
Barner-Kowollik et. al.
SS, DTC, TTC
Barner, Güven et. al.
DMAA, PEGMA, NiPAAm, TTC
Barner, Müller, Barner-Kowollik et. al.
2009
Photoinitiation
Mn2(CO)10
VAc,MA,St,DTC
Kamigaito et. al.
2013
Direct photolysis
MA,TTC
Bai et. al.
Direct photolysis
NiPAAm,TTC
Johnson et. al.
2014
PET
Fac-Ir(PPy)3
Ru(bpy)3Cl2
Various monomers
TTC,Xanthate
Boyer, et. al.
PET
Fluorescein
Eosin Y
MMA,DTB
Boyer, Xu et. al.
Monomers
Methacrylates
MMA
GMA
HEMA
DMAEMA
PEGMA
MAA
BzMA
PFPMA
Acrylates
MA
HEA
PEGA
tBA
Acrylamides
NiPAAm
DMAA
Others
VAc
NVP
St
SS
SO3 Na
Agents
Trithiocarbonates (TTC)
CDTPA
CPD-TTC
BSTP
BD-TTC
CMP
BTPA
DDMAT
Dithiobenzoates (DTB)
CPADB
CDB
CPD
PEDB
Xanthate
MESA
CPEC
MESP
Others
1-PEPDA
Dithiocarbamate (DTC)
CMPC
TETD
2015
PET
Tertiary amines
MMA,TTC
Qiao et. al.
Direct photolysis
MA,NiPAAm
CCS polymer,TTC
Qiao et. al.
Direct photolysis continuous-flow
MA,NiPAAm,TTC
Johnson et. al.
PET
PTH
NiPAAm,TTC
Johnson et. al.
Direct photolysis
VAc,Xanthate
Kwark et. al.
PET
stereo-controll
Yb(OTf)3
DMAA,TTC
Boyer et. al.
PET-PISA
Ru(bpy)3Cl2
PEGMA,BzMA,DTB
Boyer et. al.
PET
ZnTPP
TPP
NiTPP
CoTMPP
FeTMPP
MA,MMA,TTC,DTB,Xanthate
Boyer, Xu et. al.
2016
PET
Solid state amine
MMA,TTC
Qiao et. al.
PET
Bacteriochlorophyll a
MMA,BMA,DTC,TTC
Boyer, et. al.

Figure 3. Monomers, thiocarbonylthio compounds, activators, and light sources investigated to date for photo-controlled RAFT. Key research groups are acknowledged under each system. Adapted from ref.[91]

Abbreviations: VAc – vinyl acetate, St – styrene, MA – methyl acrylate, MMA – methyl methacrylate, NiPAAm – *N*-isopropylacrylamide, SS – sodium 4-styrenesulfonate, DMAA – *N*,*N*-dimethylacrylamide, PEGMA – poly(ethlene glycol) methacrylate, BzMA – benzyl methacrylate, BMA – butyl methacrylate. TETD – tetraethylthiuram disulfide, TTC – trithiocarbonate, DTB – dithiobenzoate, DTC – ditiocarbamate, CCS polymer – core-cross-linked star polymer.

6. Process of polymerization

Homogenous RAFT polymerization. As for conventional free radical polymerization, RAFT polymerization can be performed in bulk and homogeneous solution (including aqueous systems), with most of solvents used in conventional radical polymerization being applicable to RAFT, at the exception of strong nucleophilic solvents that may degrade thethiocarbonylthio group.

Heterogeneous RAFT polymerization. RAFT polymerization has also been studied extensively in various aqueous dispersed systems,[100] and it is now well established that RAFT polymerization can be conducted successfully as an emulsion or a dispersion polymerization based on a self-assembly approach. The key point is to allow formation of an amphiphilic macroRAFT agent in situ, which subsequently undergoes self-assembly into micelles leading to polymer particle formation.[101] RAFT polymerization can also be conducted successfully in miniemulsion (whereby monomer droplets are directly converted to particles). Both theoretical- and

experimental work has demonstrated that RAFT polymerization in a compartmentalized system can lead to a very significant increase in polymerization rate while maintaining good control/livingness as a result of the segregation effect on bimolecular termination.[100] This rate enhancement is a crucial feature of RAFT emulsion-based systems that enable formation of ultrahigh molecular weight polymers (See molecular weight section above). Beside polymer synthesis, the process of heterogeneous RAFT has been used to produce well-defined polymeric nanoparticles. Following self-assembly of a macroRAFT agent, chain extension with a monomer that is not soluble in the continuous phase leads to a change in the amphiphilic / hydrophobic ratio of the macroRAFT agent stabilizer, thus leading to changes in morphology of the particles, typically evolving from sphere to wormlike to vesicles. The process was coined RAFT polymerization-induced self-assembly (PISA) and can be employed in aqueous,[102] alcoholic,[103] and alternative media such as ionic liquids and super critical CO_2.[104]

Flow polymerization. An alternative process that holds promises for large scale application is the use of continuous flow reactors.[105] RAFT can be performed under continuous flow processing conditions, providing that steel tubing is used to prevent quenching of the radicals by oxygen. A key parameter to consider in this setup is the viscosity of the solution, which increases with monomer conversion and when targeting high molecular weight polymers. To date fast propagating monomers (acrylamides, acrylates, vinyl acetate) have been successfully polymerized in a range of solvents to high conversions ($Đ \sim 1.1$-1.3), at temperature ranging 70-100 ºC using trithiocarbonates and dithiocarbamates and the typical thermal initiators employed in traditional batch process.[106-107] Ambient temperature polymerization is also possible when using photoinititaion, and employing millimetre-size fluoropolymer tubing, and it enables the production of large amount (multigrams to kgs) of RAFT polymer.[108] "Quasi block" copolymers

can also be obtained by sequentially introducing monomers when the resident monomer is almost quantitatively consumed (typically 90% conversion). Upon introduction of the subsequent monomer, a gradient polymer is first formed which then evolve into a homopolymer, thus forming block-gradient-block structures.[109] Continuous flow can also be used to modify the end group of RAFT polymers, by thermolysis[110] or aminolysis.[111]

7. Industrial applications.

The RAFT process is a simple modification of a conventional free radical polymerization process by substituting a traditional chain transfer agent with a RAFT agent. It is therefore fully scaleable and does not require any special reactor setup. A survey of the current patent literature reveals over 1,000 patent applications from over 100 companies, including major international companies such as DuPont, Solvay (Rhodia), Arkema, Lubrizol, Agfa Graphics, L'Oréal, Bausch & Lomb, Unilever, etc. These patents cover a wide range of applications including microelectronics, plastic solar cells, lubricants, surface modifiers, emulsion stabilisers, paints, adhesives, cosmetics, polymer therapeutics and biosensors.

A range of RAFT agents are now commercially available, both in small quantities as special chemicals from companies such as Sigma Aldrich[112-113] and Strem Chemicals[114-115] and in larger quantities for scale-up from Boron Molecular.[116] In addition, industrial scale-up of specific RAFT agents has also been reported, including the xanthate Rhodixan-A1 by Rhodia[117] and the trithiocarbonate Blocbuilder DB[34] by Arkema and trithiocarbonate CTA-1[35] by Lubrizol.

A good example of commercial exploitation of RAFT is the Asteric™ technology developed by Lubrizol,[35] whereby sequential monomer addition in a RAFT process leads to the formation of a star polymer by the arm-fist approach. (Meth)acrylate derivatives are polymerized

using CTA-1 in a first step, followed by one-pot sequential addition of a divinyl monomer which acts as crosslinker and generate a star shape structure. The resulting materials are being produced on a multi-tonne scale, for applications in lubricating fluids for motor vehicles, as the star-shaped polymers exhibit improved viscosity index (moderate viscosity change with temperature variation) and shear stability at comparable thickening versus linear polymeric chains.

CONCLUSION

Since its first report in 1998, RAFT polymerization has gathered a tremendous momentum from both academia and industry. Nearly 20 years later, the RAFT process has now been adopted by a broad community, ranging from accomplished polymer synthetic chemists to material engineers and bioengineers, aiming at generating their own materials. With a range of versatile RAFT agents now commercially available in a variety of quantities, and industry having shown the scale up of RAFT agents and polymers is feasible, the RAFT process has now reached maturity to become a simple tool for the production of complex and functional materials.

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Funding Sources

The Royal Society Wolfson Merit Award (WM130055) and Monash-Warwick Alliance are acknowledged for financial support.

ACKNOWLEDGMENT

The author thanks his past and current research group members and all his collaborators. The reviewers of this manuscript are also gratefully acknowledged for their insightful comments and advices. The author is grateful to Dr Matthias Hartlieb for the cover art of this article.

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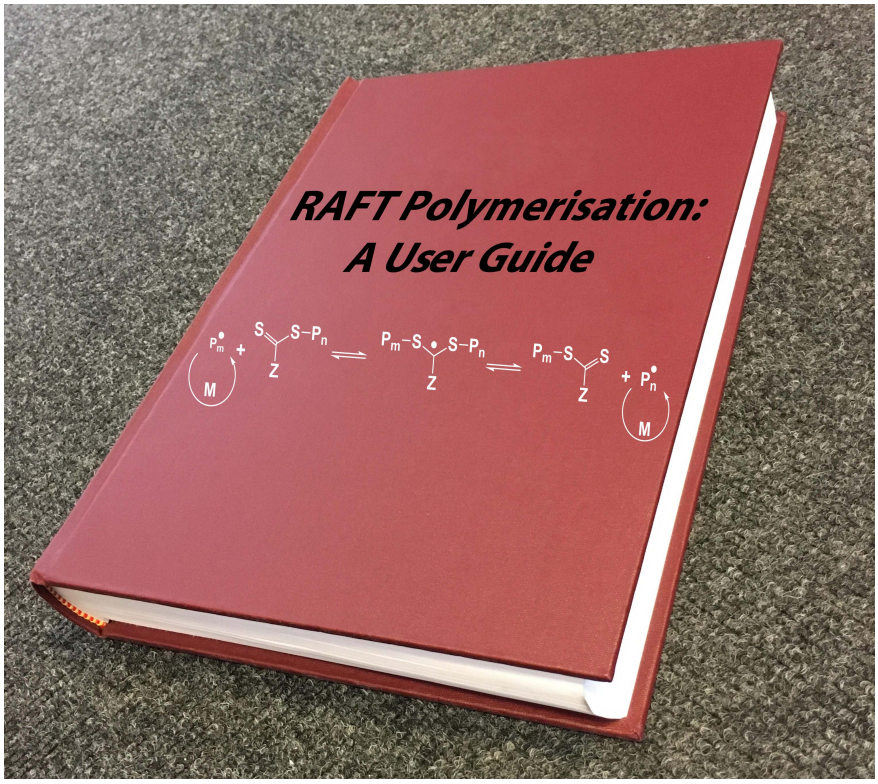
TOC Graphic



Biography

Professor Sébastien Perrier graduated from the Ecole National Supèrieure de Chimie de Montpellier, France, in 1998. He undertook his PhD at the University of Warwick, England, and spent one year as a postdoctoral fellow at the University of New South Wales, Australia. He started his academic career at Leeds in 2002 as a lecturer, then moved to the University of Sydney in 2007, as director of the Key Centre for Polymers & Colloids. In October 2013, Sébastien was appointed as the Monash-Warwick Alliance Chair in Polymer Chemistry, a joint appointment between the Chemistry Department and the Medical School at the University of Warwick, UK, and the Faculty of Pharmacy at Monash University, Australia. Sébastien's team focuses on the use of macromolecular engineering to design functional nanostructured materials, with applications ranging from material science to nanotechnology and nanomedicine. He is a member of the editorial boards of *Soft Matter*, *Macromolecules*, *European Polymer Journal, Polymers*, *Polymer Chemistry*, *Click Chemistry*, *ACS Macro Letters, ChemComm* and *ChemSocRev*. His recent awards include the Wolfson Merit Award (Royal Society, 2014), the Biomacromolecules / Macromolecules Young Investigator Award (ACS, 2014) and the IUPAC / Samsung Young Polymer Scientist Award (IUPAC, 2014).